

COLOR-PHOTOGRAPHS OF THE PHOSPHORESCENCE OF CERTAIN METALLIC SULPHIDES.

BY EDWARD L. NICHOLS.

(Read April 14, 1916.)

Among the most beautiful and interesting of phosphorescent substances are the sulphides prepared and described several years ago by Professors Lenard and Klatt,¹ of Heidelberg. These substances which consist of the sulphide of barium, calcium or strontium, with a small admixture of some metallic salt—usually of copper, bismuth or lead—are prepared by heating with a flux such as sodium sulphate, sodium borate or lithium phosphate. After exposure to daylight or to violet or ultra-violet rays they glow for a considerable time with characteristic colors which depend upon the particular mixture used.

Variations in the brightness of phosphorescence with the time find convenient indication by means of the curve of decay and the effects of temperature, etc., on the intensity are likewise capable of graphic or analytical expression. These relationships have already been extensively studied by the authors just cited and others and in a paper read before the American Philosophical Society in April, 1910, I presented the results of such an investigation. The subtle and fleeting changes of color which occur as the phosphorescence dies away or when the substance is heated or cooled or when we compare sulphides varying in composition, do not lend themselves to such methods of expression. The effects must be seen to be appreciated and it seemed of interest to try to record some of the phenomena by means of color photographs.

Now the glow of even the brightest of these phosphorescent substances is in reality of very low intensity and color-plates such as the Lumière plates used in the experiments to be described are relatively

¹ Lenard and Klatt, *Annalen der Physik*, 15 (1904), also Lenard, *ibid.*, 31, p. 641 (1910).

slow. The total light effect obtained by a single excitation is inadequate for the proper exposure of the plate when used in the camera in the ordinary manner. Indeed it was found in some preliminary trials by Professor G. S. Moler and the writer that a plate placed in immediate contact with a tube containing the phosphorescent sulphide as soon as practicable after intense excitation and allowed to remain for several minutes or until nearly the whole of the total light effect had been utilized, was decidedly under-exposed.

On the other hand the color effects to be recorded change rapidly, especially during the first few hundredths of a second after excitation so that it was necessary to obtain the equivalent of a large number of successive short exposures each made at the particular time after excitation for which the color record was desired.

To this end a special form of phosphoroscope² was constructed by means of which the substance, enclosed in a flat tube of glass about 10 cm. long and from 1 cm. to 1.5 cm. wide, was viewed through a revolving disk with alternate open and closed sectors of 45° aperture. The disk was mounted on the shaft of an alternating current synchronous motor on a 60-cycle circuit and excitation was by a series of five sparks (*E*, Fig. 1) between zinc terminals.

The sparks were produced by the action of the secondary coil of a small step-up transformer with condenser *C*, in the same circuit.

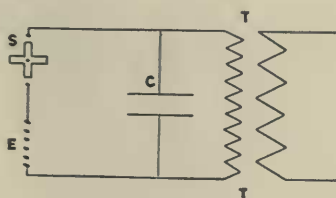


FIG. 1.

A spur wheel of zinc (*S*) was mounted on the shaft of the motor and its four arms passed the two terminals of the sparking circuit with an air space of about 1 mm. The wheel was adjusted so that this passage coincided with successive crests of the alternating-cur-

² See a paper presented by Nichols and Howes at the meeting of the Am. Phys. Society, Washington, April, 1916, abstract *Physical Review* (2), VII., p. 586, 1916.

rent wave and the sectored disk was shifted until the sparking occurred during eclipse, *i. e.*, at the time when a closed sector obscured from view both the sparks and the substance under excitation (see Fig. 2, position 1).

With this arrangement the specimen, which was mounted vertically in a line parallel to the row of spark gaps and distant from them about 2 cm., was intensely illuminated 120 times a second and was visible during intermediate intervals of $1/240$ of a second, each

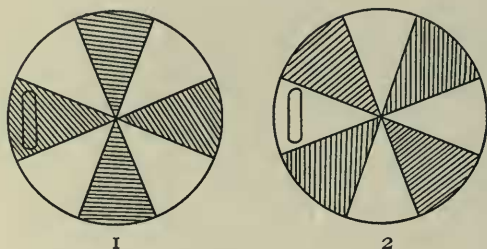


FIG. 2.

beginning about .0001 second after excitation ceased (see Fig. 2, position 2).

For observations during later stages of decay the wheel could be driven slowly by means of a direct-current motor or moved stepwise an eighth of a revolution at a time at the desired rate.

Since some of the most striking changes of color are produced by differences of temperature, the tube containing the phosphorescent sulphide was mounted within a cylindrical Dewar flask with un-silvered walls. The lower end rested in a metal mercury cup while the upper end passed through a heating coil (see Fig. 3). From the bottom of the mercury cup, *M*, a copper rod projected downwards into liquid air. The region at *A* could thus be maintained at a temperature of $+20^{\circ}$ C., or higher, while the lower end at *B* was at approximately -185° C.

A fairly stable temperature gradient soon established itself and the colors of phosphorescence through the entire range could be observed and photographically recorded.

Excitation under these conditions was obtained by inserting the sparking device within the Dewar flask and many photographs were made in that way; but this is a procedure demanding special pre-

cautions, as the atmosphere above the liquid air is very rich in oxygen and conflagration of the insulating materials and even the metal parts is likely to occur.

The principal phenomena to be studied were those due to:

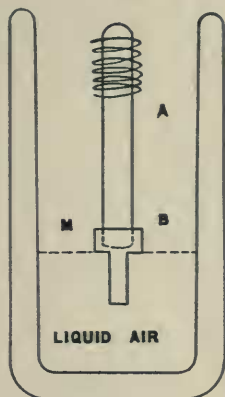


FIG. 3.

1. The change of color during the decadence of phosphorescence.
2. The effect on the color of phosphorescence when excitation occurs at temperatures between $+20^{\circ}$ and -185° .

CHANGES DURING DECAY.

To confirm the well-known phenomenon of change of color during decay it is only necessary to mount one of the sulphides in the phosphoscope and excite with the disk running at normal speed, *i. e.*, 1,800 rev. a minute. The appearance as viewed through the revolving disk is then that due to its phosphorescence during the interval .0001 to .004 second (approx.) after excitation. If the excitation be stopped by breaking the spark circuit the changes of color as phosphorescence dies away can be followed for several seconds.

In the case, for example, of a sulphide known as No. 33 (Ba, Cu, $\text{Na}_2\text{B}_4\text{O}_7$) the initial tint of red-yellow changes to a deep red. Another preparation, No. 3 (Ca, Bi, Na_2SO_4 ; $\text{CaF}_2\text{Na}_2\text{B}_4\text{O}_7$), which is typical of many, appears bluish green through the rapidly revolving disk and changes very rapidly after the close of excitation to a deep

violet. (Photographs were shown at the meeting illustrating these and similar cases.)

The work of Lenard and others using a very different procedure has shown the spectra of these substances to consist of broad overlapping bands distinguishable from each other chiefly by the mode of excitation, duration, and the influence of temperature and it is clear that in these and similar cases we have to do with two or more such bands.

In the first of these two examples the change of color may obviously be explained by the more rapid decay of the band of shorter wave-length; an hypothesis readily verified by observing the substance as seen through the disk with a spectroscope. What appears as a single very broad band collapses promptly from the green end when the exciting circuit is broken, leaving the red portion only, which persists for many seconds.

We have to do then with a combination of a band of very short duration (having its crest in the green) and a band of long duration in the red and the color at any time after the close of excitation is the sum of the instantaneous values of the two components.

Since the decay of the green band is very rapid indeed, its intensity becoming negligible in a small fraction of a second, the appearance of the phosphorescent surface when observed by ordinary methods is chiefly due to the red component and it appears of a much more ruddy color than when viewed through the rapidly revolving disk. The same is true of all the other barium sulphides studied.

The Ca and Sr sulphides in general appear as greenish blue, pure blue or even violet as in the example cited (No. 3) when viewed in the ordinary manner; but in the phosphoscope they are green, going over into blue or violet after the cessation of the periodic excitation. Here obviously we again have to do with two bands of which the green is of very short duration, while it is not in this case the band of longer wave-length which persists but that of greater refrangibility. It appears in general that these sulphides fall into two distinct classes: Those of which the persistent band is of longer wave-length, *i. e.*, red, chiefly if not exclusively barium

sulphides, and those of which the persistent band is of shorter wavelength.

Thirty-four sulphides examined by the method already described showed color changes in accordance with the foregoing classification.

COLOR CHANGES DUE TO COOLING.

Since the intensity of the band of rapid decay vanishes in a small fraction of a second, ordinary observations of the phosphorescence of these sulphides pertain, as has already been pointed out, to the persistent band alone. It is not possible moreover to isolate the rapid band by the use of the phosphoroscope, since during the brief period immediately following excitation we have both bands present and the color due to their combination.

The slow bands, however, are greatly diminished in intensity by cooling the phosphorescent substance and are often reduced almost or quite to the vanishing point. Thus it is possible by lowering the substance during the experiment to temperatures approaching that of liquid air, to observe the color and intensity of the rapid band, by itself.

When we cool the lower end of a tube of the BaCu sulphide No. 33 with liquid air, as described in a previous paragraph, and observe

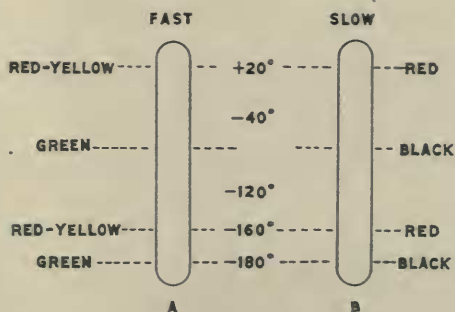


FIG. 4.

its phosphorescence through the sectored disk, the red-yellow of the upper (warm) end merges gradually into a brilliant green occupying the cooler regions below. A red-yellow patch occurs still lower down, while at the very bottom where the temperature approaches

that of liquid air there is a return to green. The distribution of colors and approximate temperatures are indicated in Fig. 4 (*A*).

That this remarkable distribution of colors is to be interpreted as the result of the killing off of the "slow" red band by cooling and its subsequent recurrence at about -160° , is beautifully confirmed by the appearance of the tube after the entire cessation of excitation. When the spark circuit is broken, the green vanishes at once but the red regions above and below continue to glow for many seconds as indicated in Fig. 4 (*B*).

In 1910 I measured the change in the phosphorescence of this substance³ effected by temperature. The curve, which is reproduced in Fig. 5, applies to the red band only, since the green band would have vanished long before observations of brightness could be made

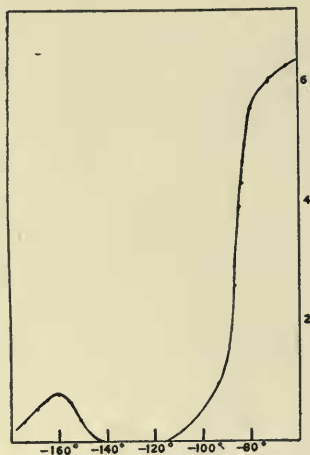


FIG. 5.

by the method then employed. It describes exactly the appearance noted in Fig. 4*B*, *i. e.*, a rapid diminution on cooling, complete disappearance at about -120° C., a recurrence of measurable intensity below -140° with a maximum at -160° .

All BaCu combinations, so far as examined, have a red-yellow color of phosphorescence at room temperature with the red band of longer duration, but the relative intensity of the red varies greatly

³ *Proc. of Am. Philosophical Soc.*, XLIX., 275, 1910.

with different fluxes and proportions. While the persistence of the green band at low temperatures seems to be a general property of these substances the recrudescence of the red as in the example here considered is not so apparent in other cases. In the other substances of this class it must be regarded either as masked by the brightness of the green component or entirely absent. In the former case one might expect a modification of the green at the temperature in question and in several specimens thus far studied this is clearly the case.

The effect of cooling the phosphorescent sulphides of calcium and strontium is analogous to that just described.

The band of long duration is greatly weakened or disappears;

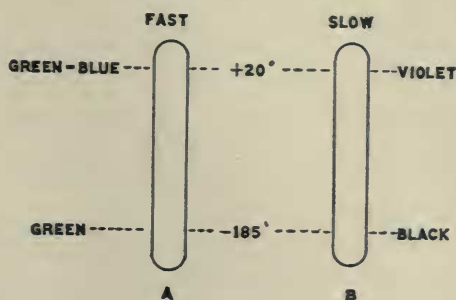


FIG. 6.

the other, which in all these cases, so far as has been observed, is a green band, persists.

Since the band destroyed by cold is, however, blue or violet, the change of color is in the opposite direction from that noted in the case of the barium compounds, *i. e.*, from blue or blue-green to green instead of from red-yellow to green.

The most striking example in this class is perhaps the combination (Ca, Bi, Na_2SO_4 ; CaF_2 , $\text{Na}_2\text{B}_4\text{O}_7$) already referred to. The greenish blue of early phosphorescence, as observed through the sectored disk at $+20^\circ$, goes over to a full green of short duration in the cold portions of the tube, the phosphorescence of long duration being in both cases of a remarkably rich pure violet. See Figure 6.

It is obvious that the methods described in this paper bring out from quite a new standpoint the structure of the phosphorescence

spectra of these sulphides and enable us not only to record the changes of color but to explain them.

Many interesting points are still to be determined which are likely to have a bearing upon the theories of luminescence.

It will be possible for example, having shown that the bands of short duration are really separable by cooling from the components of slow decay, to locate these properly by the use of the spectrophotometer and phosphoroscope.

We shall then know whether the green band which persists at low temperatures is the same for all the sulphides or, as is more likely, varies in position and character with the compound employed; in what manner the components of long duration depend on the composition; whether the loss of brilliancy which many of these substances undergo with age, affects both sets of bands, etc.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY,
April, 1916.